

# REPORT DOCUMENTATION PAGE

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# **FINAL PROGRESS REPORT**

## **MECHANISMS OF PHOTOREFRACTIVITY IN POLYMERIC MATERIALS**

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submitted by

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## 2. Objectives:

To develop advanced photorefractive (PR) polymers for future optical processing applications with higher speed, larger response, and infrared sensitivity, we will utilize organic synthesis and physical measurements to understand and thereby control the properties of photoinduced charge generation, photoconduction, optical nonlinearity, and trapping dynamics.

## 3./4. Status and Accomplishments/New Findings:

### Synthetic and Physical Studies: New charge-transporting host polymers based on poly(siloxane)

Most photorefractive polymer (PRP) composites have used poly(n-vinyl carbazole) (PVK) as the polymer matrix and charge transporting medium. PVK has many advantages, including its commercial availability, the depth of study on the polymer, and its ability to dissolve polar chromophores. Almost all the progress in the field has been accomplished with materials using this polymer, but PVK also has several disadvantages. In light of the discovery of the "orientational enhancement" effect, there is much to be gained in terms of index contrast if the  $T_g$  of the composite is close to room temperature. Unfortunately, the intrinsic  $T_g$  of PVK is above 200 C, and an additional plasticizer must be added. The addition of plasticizer can be deleterious since it wastes volume in the sample, can lead to phase separation, and can effect the PR dynamics, often in ways that are difficult to understand. We sought to solve several of the above problems simultaneously by characterizing the following polymers synthesized by Mike DeClue and Prof. Jay Siegel, UCSD:

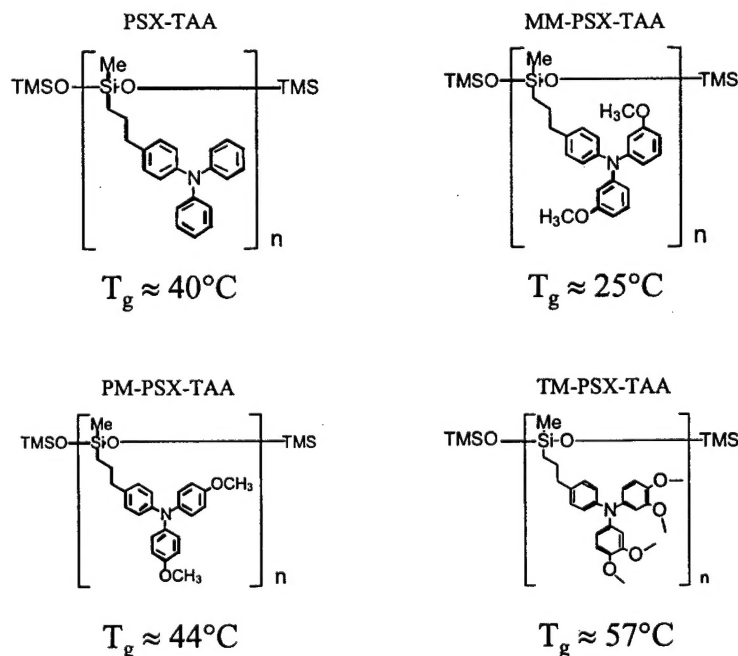
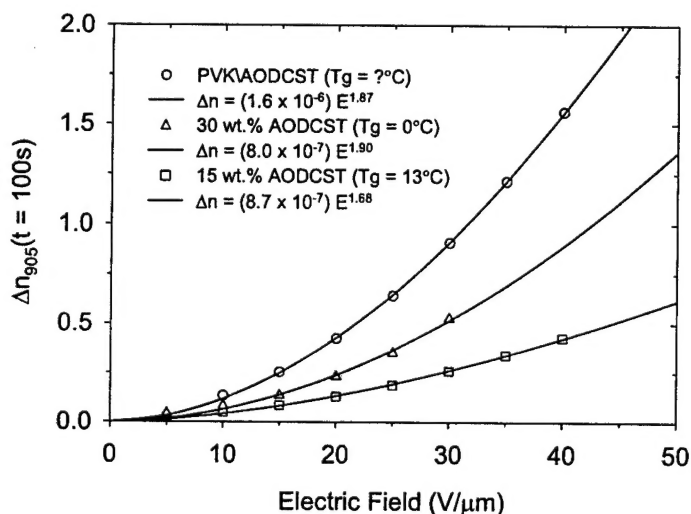


Figure 2.2: Chemical structures of four PSX-TAA derivatives

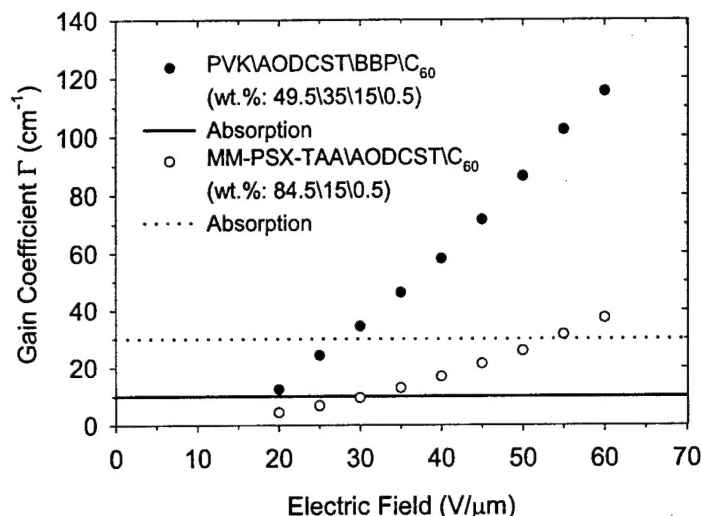
As one can see, the poly(siloxane) backbone has a much lower  $T_g$  than that of PVK. The xerographic community has studied the tris-tolylamine (TTA) monomer, and when doped into polystyrene, mobilities up to  $10^{-4}$  cm<sup>2</sup>/Vs have been measured. TTA also has a lower oxidation potential than carbazole. Thus this combination of a better charge transport agent with a polymer that does not require additional plasticizer could lead to an improved composite. The additional methoxy groups were added to improve the solubility of polar chromophores in the matrix. We were able to make composites with these materials without any additional plasticizer. The best results were obtained with composites of MM-PSX-TAA\AODCST\C<sub>60</sub>, which are described below.

Transient ellipsometry is a technique commonly used to probe the orientational dynamics of chromophore in PR polymers. The technique can allow one to sense the time dependence and magnitude of the refractive index change created by the poling of the chromophores by an external electric field. These experiments were used to quantify the orientational characteristics of the chromophores in the new composite. The quasi steady state results (after 100 seconds) are shown below.



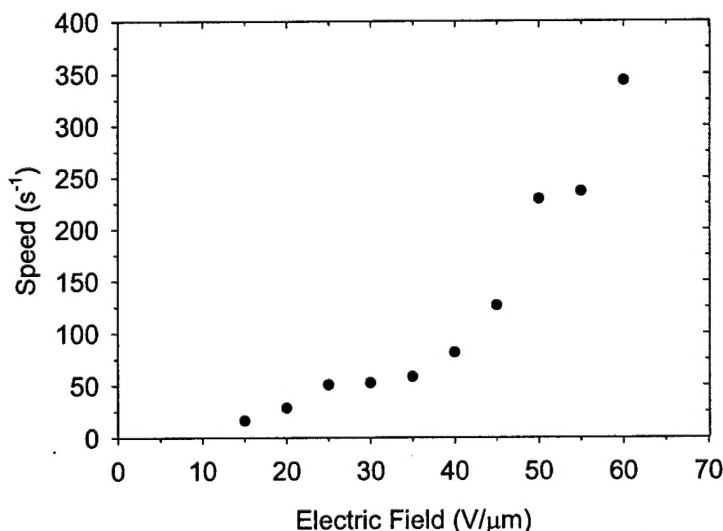
Electric field dependence of the quasi steady state refractive index change.

In this figure we compare the electric field dependence of the refractive index change in samples of PVK\AODCST\BBP\C<sub>60</sub> (49.5\35\15\0.5 wt. %, upper curve, where BBP is butylbenzylphthalate), MM-PSX-TAA\AODCST\C<sub>60</sub> (69.5\30\0.5 wt. %, middle curve), and MM-PSX-TAA\AODCST\C<sub>60</sub> (84.5\15\0.5 wt. %, lower curve). As can be seen in this figure, there is a reduction of the quasi-steady-state magnitude of the nonlinearity by about a factor of two between the PVK composite and the PSX material, even though the wt. % of the chromophore is the nearly the same, and about a factor of three when we use 15 wt. % of AODCST. We can only conclude that the difference is due to AODCST occupying a smaller volume fraction in the PSX-TAA composite. We also observe a factor of three difference in the non-linearity between PVK\AODCST\BBP\C<sub>60</sub> and MM-PSX-TAA\AODCST\C<sub>60</sub> (84.5\15\0.5 wt. %) when comparing steady-state refractive index changes measured by four wave mixing (FWM) (data not shown) and in the steady-state gain coefficients in two wave mixing (TWM) experiments:



TWM gain coefficient comparison of PSX-TAA and PVK samples

When we compare the speeds of the PSX-TAA and PVK composites, the PSX-TAA composite has about a factor of three larger speed at equivalent experimental conditions. As can be seen in figure below, average speeds of several hundred inverse seconds can be obtained at fields below 60 V/μm:



Averaged photorefractive speed comparison of MM-PSX-TAA/AODCST/C<sub>60</sub> vs. applied electric field at a writing intensity of 1 W/cm<sup>2</sup>.

In conclusion, these new polymers have several attractive features as compared to the standard PVK, including no need for additional plasticizers and possibly higher hole mobility. We observe a reduction of non-linearity when using the chromophore AODCST, probably due to reduced volume fraction of the chromophore in the PSX-TAA samples. The photorefractive speed was similar to the best one can achieve with PVK composites, which puts the new PSX-TAA among those PRP polymer materials with the highest speeds reported to date.

## 5. Personnel Supported:

Graduate students: Daniel Wright, Eric Elliott, Michael DeClue

## 6. Publications:

153. A. Grunnet-Jepsen, D. Wright, B. Smith, M. S. Bratcher, M. S. DeClue, J. S. Siegel, and W. E. Moerner, "Spectroscopic Determination of Trap Density in C<sub>60</sub>-Sensitized Photorefractive Polymers," *Chem. Phys. Lett.* **291**, 553-561 (1998).
182. D. Wright, U. Gubler, S. Sadhukhan, W. E. Moerner, M. He, R. J. Twieg, M. DeClue, and J. Siegel, "Organic Photorefractive Material Design Strategies," *Proc. Soc. Photo-Opt. Instrum. Engr.* **4462**, 125-138 (2001).
201. D. Wright, U. Gubler, W. E. Moerner, M. DeClue, and J. S. Siegel, "Photorefractive Properties of Poly(siloxane)-triarylamine-Based Composites for High Speed Applications," *J. Phys. Chem. B* **107**, 4732-4737 (JP027456i, 2003).